ON THE CONDUCTION OF ELECTRICITY AT CONTACTS OF DISSIMILAR SOLIDS

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INTRODUCTION.

THE fact that the resistance to the flow of current across the contact of dissimilar solids depends upon the direction of the current was first observed by Ferdinand Braun[1] in 1874, with metallic sulphides against metals. Braun showed later, 1877–8, that the effect was not due to counter E.M.F. of polarization, as the sulphide suffered no change in weight. Also, current from the secondary of an induction coil passed simultaneously decreased the resistance in both directions.

The more recent contributions to the subject have been inspired, in most cases, by the application of such unilaterally-conducting contacts, usually called "crystal rectifiers," to the detection of electromagnetic waves. The name comes from the fact that contacts having this property are usually those between a metal and a crystalline substance. Many such crystals are known. Among those which have been most carefully studied are the silicon-steel, carbon-steel, and aluminium-tellurium rectifiers of L. W. Austin.[2] The first gave phenomena, very reproducible below 0.2 volt, A.C.; the direction of the rectified current being from steel to silicon, except with one specimen which gave opposite rectification for all points on the surface. In every case the thermo-E.M.F. was opposite to the rectified E.M.F.

The carbon-steel rectifiers were made by placing a steel needle in contact with a cored arc-light carbon. Graphite was found unsatisfactory. A lamp filament against a light carbon also furnished a satisfactory rectifier. The phenomenon was not, however, regular with direct current. The rectified current was from steel to carbon.

The aluminium-tellurium rectifier, discovered previously by Austin,[3] exhibited a marked peculiarity. For low voltages, up to 0.6 volt, 8.0 amperes, the rectified current was in the direction of the thermo-E.M.F.; *i. e.*, Al to Te; whereas above this voltage, the rectified current was in the opposite direction, and increased with increasing voltage. Large contacts, such as a No. 20 aluminium wire melted into a block of tel-

[1] Ferdinand Braun, Pogg. Ann., 153, p. 556, 1874.
[2] L. W. Austin, Bull. Bur. Standards, 5, 1, pp. 133–147, 1908.
[3] L. W. Austin, PHYS. REV., 24, pp. 508–520, 1907.

lurium, gave marked unilateral conductivity with direct, but unsatisfactory rectification with alternating, currents.

An extensive series of experiments has been undertaken by G. W. Pierce. The first piece of work[1] was on the carborundum rectifier. The resistance of this substance is much higher than that of those just described, so that a rectified current of the order of 10^{-3} amperes requires an E.M.F. of 20 volts. With a pressure on the crystal of 500 grams, one specimen gave a rectification of 4,000 : 1. On increase of pressure the resistance fell in both directions but the rectification, *i. e.*, the ratio, decreased. There was still some rectification, however, even when the crystal was driven well into the electrode. Best results were obtained when one of the surfaces of the crystal was platinized, to give low resistance, the rectified current then being in the direction of crystal to metal. With a current of ½ ampere, the rectification was but 1.6 : 1.1, the crystal grew hot, and the contact surfaces luminous. The temperature coefficient of resistance of carborundum resembles that of a salt solution more than that of a metal.

An hysteresis effect was observed, apparently due to a slow building-up of the current, which disappeared after a few reversals—the current on rise of E.M.F. being less than on return to zero. An attempt was made to observe a back E.M.F. The rectifier was connected alternately, 120 times a second, with a source of potential of 35 volts, and a capillary electrometer. A persistent but very small reading, 0.002 volt, was indicated.

The second piece of work[2] was performed with certain minerals—brookite, anatase, and especially molybdenite. For each of these the rectified current was from metal (usually copper) to crystal, and of the order of 0.01 ampere for 10 volts. The extent of the rectification depended upon the circumstances of contact, as regards position on the surface of the crystal, and pressure at the point.

Of particular interest were the experiments with molybdenite, undertaken to show, by oscillographic records, the existence of a counter E.M.F. existing for a short period of time. The apparatus consisted of a Braun tube, the luminous spot of which was focused on a sensitive film on a rotating drum. This drum was driven in synchronism with the current which passed through the rectifier and the deflecting magnets of the Braun tube. The drum was revolved until successive exposures had combined to give a sufficient intensity to the film. These oscillograms showed that the rectified cycles led their respective voltage-phase

[1] G. W. Pierce, Phys. Rev., 25, pp. 31–60, 1907.

[2] G. W. Pierce, Phys. Rev., 28, pp. 153–189, 1909.

cycles at three positions. But these could be obtained by calculation, from the resistance and inductance of the circuit. In fact, no departure in amplitude or phase existed between the rectified cycle and the voltage-phase (applied) cycle that was not accounted for by the inductance of the oscillographic apparatus, or by the current-voltage curves of the rectifier with steady currents. In other words, if there were any terms contingent upon heating or other effects which involve an integral of a function of the current with respect to the time, this integral attained its final value in about 1/6,000 second, corresponding to about 1 mm. on the original photograph.

In a further piece of work,[1] Pierce examined the rectifying properties of iron pyrites. This substance had been studied previously by Braun, who found that the difference in the conductances in the two directions increased with increase of current; and with continued passage of the current, the larger conductance decreased. Pierce found this only with currents large enough to heat the contact.

The oscillograms, like those taken with the molybdenite rectifier, showed that the current through the rectifier had the same phase and amplitude it would have if the rectifier were replaced by a resistance producing the same amplitude, *i. e.*, there was no apparent integrative action. This rectifier showed the irregular action manifested by all the solid rectifiers previously investigated, namely, that for some adjustments of the contact, the greater current was from copper to crystal, whereas for other adjustments, *e. g.*, with a different pressure, or at a different point on the crystal, the greater current was from crystal to copper. With fixed adjustments, the current and E.M.F. were constant.

A study of the galena rectifier has been made by A. E. Flowers.[2] When the E.M.F. is gradually increased from a low value, "break-downs" occur; *i. e.*, the current jumps suddenly to a higher value. If the E.M.F. is further increased, a large jump of current eventually occurs, the metal point sinks into the galena, and rectification is destroyed. These break-downs occur more frequently if the E.M.F. is reversed at each increase, and the contact will stand a rather high E.M.F. if it is removed temporarily, as soon as the breakdown occurs.

In confirmation to Pierce's observations, certain parts of the galena crystal were found to be non-rectifying. Further "a non-rectifying surface was often found to have others beneath and parallel, when layers were split off, but scratching or scarring a surface usually spoiled more or less completely its rectifying properties." Heating destroyed the

[1] G. W. Pierce, Phys. Rev., 29, pp. 478–484, 1909.

[2] A. E. Flowers, Phys. Rev., 29, pp. 445–560, 1909.

effect, although it was sometimes regained by further heating, disappearing again as the temperature was still further increased. The effect did not depend upon the metal at the contact.

The author emphasizes the time taken to build up the current on closing the circuit, observed with some crystals, especially on heating. It was found that an artificial rectifier could be made by allowing sulphur to burn on the end of a copper wire for a moment, and afterward placing this sulphur against lead (brass was unsatisfactory) and reversing a current through the contact a few times.

Few theories of the foregoing phenomena have been suggested. The effects were first thought to be of thermoelectric origin but Austin and Pierce showed that heating could not account for the magnitude of the effects observed. Pierce[1] considers that all rectifiers come under more or less the same class of phenomena, and that there may be some connection between thermo-E.M.F. and rectification, as all rectifying crystals have large thermo-E.M.F.'s against the common metals. Flowers concludes that the effect, with galena, is due to electrochemical deposition of a resisting film.

Allied Phenomena.

Closely related to the crystal rectifier is the electrolytic rectifier—a fine platinum wire touching the surface of an electrolyte. Although the contact area is of the same order, there are two marked differences; oscillograms made by G. W. Pierce[2] show evidence of a positive E.M.F., for about 1/1,500 second, greater than the E.M.F. immediately following; further, for best results, a steady current should be superposed on the alternating current to be rectified. Austin[3] considers that heat is one of the factors, with, probably, chemical action and electrostatic attraction across the gas film.

The aluminium valve, or rectifier, which consists of a cell containing one of certain electrolytes, one electrode being an aluminium plate, is more amenable to experiment than the rectifiers previously described, owing to its size. The hindrance to the passage of the current has been shown[4] to be due to back E.M.F. This is produced slowly on a fresh plate, 10 minutes being required to obtain the full valve effect at 15 volts. Increase of temperature decreases this E.M.F. Careful experiment[5] has shown that the back E.M.F. together with the drop due to ohmic resistance is equal to the total impressed voltage even when the latter is 20

[1] G. W. Pierce, Phys. Rev., 29, pp. 478–484, 1909.

[2] G. W. Pierce, Phys. Rev., 29, pp. 56–70, 1909.

[3] L. W. Austin, Bull. Bur. Standards, 2, pp. 201–224, 1906.

[4] S. R. Cook, Phys. Rev., 15, p. 23, 1904.

[5] S. R. Cook, Phys. Rev., 20, pp. 312–321, 1905.

or more volts. On removing this applied voltage, the counter E.M.F. falls off to about half its value in 10 seconds.

There are two suggested explanations for the low resistance of the valve when aluminium is cathode. Guthe[1] suggests that hydrogen ions are liberated between the film and the metal, and these can pass through the more or less solid film of Al_2O_3 on the metal, whereas, when the current is in the opposite direction, the large negative ions from the solution cannot penetrate this film. Schulze[2] considers that the solid film merely serves to hold a gas between it and the metal. Electrons from the metal can pass readily through this gas whereas the large negative ions from the solution meet with resistance. This view is more or less supported by experiments made under pressure[3] which show that the rectification becomes less, temporarily, under pressure. When the gas is condensed, there should be less distance for the large ions to travel.

Many coherer phenomena suggest strongly that films play an important part in conduction at small contacts. This is very evident in some cases. For example, very sensitive coherers are formed[4] by lead in contact with *oxidized* copper, or copper alloy. Eccles[5] has advanced the theory that the action of iron-mercury, and oxidized iron-iron coherers depends entirely on the heating of the film of oxide by the electrical oscillations and the current due to the applied p.d. By developing the theory mathematically the necessary results are shown to follow. Further, it has been found[6] that a platinum wire placed upon two others coheres, if an oscillatory spark is set up in the neighborhood. The same effect may be produced with a broken carbon filament in an incandescent lamp globe, provided a considerable resistance is placed in series. The coherence of the platinum wires may also be produced by heating each junction to a red heat.

In certain other cases, the rôle of the film is not so evident. For example[7] a tantalum wire, 0.05 mm. in diameter touching mercury forms a very sensitive coherer, which cannot be made permanently to cohere. Further, Shaw and Garret[8] have found that when a coherer formed of two copper wires touching each other is made to cohere by a spark some distance away, the wires if separated (requiring a small but measurable pull) and held apart for a few moments will not recohere when

[1] Guthe, Phys. Rev., 15, p. 327, 1903.

[2] Schulze, Ann. der Physik, 28, p. 787, 1909.

[3] Carman and Balzer, Phys. Rev., 30, pp. 776–781, 1910.

[4] M. Hornemann, Ann. der Physik, 14, 1, pp. 129–138, 1904.

[5] W. H. Eccles, Phil. Mag., 19, pp. 867–888, 1910.

[6] Majoli, N. Cimento, 10, pp. 552–585, 1905.

[7] L. H. Walter, Proc. Roy. Soc., Ser. A, 81, pp. 1–8, 1908.

[8] Shaw and Garret, Phil. Mag., 8, p. 164.

placed together again, but will do so if the current be reversed. The wires may again be separated and the action repeated several times.

Study of Various Contacts.

In the present investigation it seemed advisable to try a number of rectifying substances against various metals, in order to see if any general conclusions could be drawn. The apparatus consisted simply of a source of E.M.F. of one or two volts, connected through a small resistance to a milliammeter and a switch which served to reverse the current passing

Substance.	Greater Current Flows from —		Conductances Diverge.		Conductances Approach.	
			The More Rapid Change is the—			
	Metal to Crystal.	Crystal to Metal.	Rise.	Fall.	Rise.	Fall.
C	Al	Pb			Si	
	Fe	Si				
Te		Mg	Mg	Cu		Na
		Al	Al	Pt		
		Zn	Zn	Si		
		Cu	Pb			
		Fe	Ag			
		Ag	Galena			
		Sn				
		Pb				
		Pt				
		Si				
		Galena				
Si	Al		Pb	Al		
	Zn		Pt	Zn		
	Cu			Cu		
	Fe			Fe		
	Sn			Sn		
	Pb					
	Pt					
Galena	Cu	Al		Al		Cu
	Fe	Sn		Zn		Si
	Pb	Ag		Cu		
	Pt	Si		Fe		
		Zn		Pb		
				Pt		
Magnetite	Zn	Al		Pb		Zn
	Pb	Cu		Te		Cu
	Pt	Ag		Si		Pt
	Te	Si				

through the rectifier. The drop across this switch was measured by a voltmeter with a range of three volts. Direct current was used in order to bring out any gradual change that might appear while the current was being applied. Where there was uncertainty regarding the direction of the rectified current, a number of contacts were made to determine the general direction.

The result of these experiments is given in the following table, in which certain general tendencies are apparent. The conductances, in most cases, grew farther apart the longer the current passed, the rise being more rapid with some metals and the fall with others, as the table indicates.

While the current was passing the conductances usually changed together; *i. e.*, while one was rising or falling, that in the opposite direction was rising or falling, as could be seen by sudden reversals. This was not always true, as one conductance sometimes remained stationary. Usually the conductance in the direction which had undergone greater change recovered the faster. Scraping a metal to remove possible oxide sometimes increased the mean conductance but decreased the difference.

Permanent Changes of Conductance.

The gradual changes that have just been described are indicative of something like a change of structure at the contacts, due to the passage of the current, and an attempt was made to learn if the conductance of the contact was the same after current had passed in either direction. To test this point, rectified currents of the order of 1×10^{-2} amperes were passed through the contact, which could be immediately connected is series with a galvanometer and a high resistance, so that a current would pass of the order 1×10^{-5} amperes, which did not produce rectification.[1]

The current due to thermo-E.M.F. was eliminated by reversing the current through the contact and taking the mean value. The difference in the deflections, after the larger current had passed in one direction or the other, varied up to about 30 per cent. of the lesser, depending somewhat on the circumstances of contact. The deflections were for the most part steady, and were, for most substances, greater after the current had passed from metal to crystal, as the following table will show.

That these changes of resistance, indicated by galvanometer deflections, did not take place instantly was shown by passing the larger current

[1] Throughout this paper, excepting the part that deals with the oscillographic study, the "rectification" was measured by applying a direct current, first in one direction and then in the other direction, the time of application being long enough to take a reading of the current.

in one direction, then noting the deflection with the smaller current—for example Te to Fe_3O_4, deflection 13.8—then "making" the larger current in the opposite direction for very short intervals, by letting the ends of two wires touch while moving rapidly past each other—giving, successively, deflections, 13.2, 12.6, 12.0, the last being the same as that obtained for this direction previously. In some cases, for example, PbS, Zn, the deflections after long exposure to current were less than after a shorter exposure.

Substance.	Deflection Greater After Current has Passed from	
	Metal to Cr stal.	Crystal to Metal.
Te	Fe Pb Pt Si Galena	Al
Si	Al Cu Fe Si	Zn Pb Pt
Galena	Al Zn	Pt Si
Magnetite	Al Fe Pb Pt Si	Zn Te Galena

Before the larger current was first applied, the deflection was usually smaller than afterward, and in certain cases was not steady, there being a slow rise or fall of deflection irrespective of whether the small current were on o1 not. The effect was not of a very definite nature and seemed to depend upon the circumstances of contact. Most of the substances and metals gave steady deflections; those showing a fairly certain rise and fall respectively were: Fe_3O_4, Pb; Fe_3O_4, Si; PbS, Te; Si, Si; and Te, Pt; Fe_3O_4, Pt; PbS, Zn. The effect is very similar to a spontaneous rise observed by the writer in studying the conductivity of powders,[1] namely, for powdered BaS.

Effects with Large Currents.

In considering the general effects by currents of from 0.5 to 9 amperes, it will be convenient to call the direction of current from metal to crystal,

[1] R. H. Goddard, Phys. Rev., 28, p. 411, 1909.

A, and the reverse direction, B. In most cases the current in the direction A showed the greater irregularity, the current in the direction B being perfectly steady in some experiments. An exception was C, Fe_3O_4, for which the current in direction A took steadily the largest value B attained in its frequent jerks. These irregularities for A were of a definite kind, with some contacts. For example, with galena against Cu, Ag, Pb, Pt, and once with Te, Pt, the current kept falling gradually and then rising with a jerk. With Si, Zn; Si, Pb; and PbS, Ag, these irregularities were accompanied by acoustic effects. In the first two contacts a hissing noise accompanied the passage of current in the direction A, while there was silence for B, except for occasional clicks. The PbS, Ag contact emitted a musical trill for the direction A. Also, with other contacts, there was occasionally a click on opening the circuit, and on reversing.

During the passage of a large current, there was visible sparking for the direction A, most noticeable with Te, Al; Te, Mg; Te, Zn, but lacking with Te, Ag; and Si, Al. Also, if the contact was glowing, the color was usually brighter for the direction A, especially with Si, Al; Si, Pt; Si, Zn; Te, Zn; Te, Al; but duller with Fe_3O_4, Al; Fe_3O_4, Zn. The portions of some substances close to the contacts showed colored deposits after the passage of considerable current. With Si, Zn the color was yellow, with C, Al, white, and with Fe_3O_4, reddish.

The direction of greater current, *i. e.*, of rectification, changed in many cases when the current was increased to 0.5 ampere or more, the general tendency being to change from the direction A to B. Tellurium, for which the rectification is in this direction, gave no change on increase of current, with any metal. Silicon exhibited this change with Al, Ag, Fe, Zn, and Pt, with currents equal to and greater then 0.45, 1.3, 0.50, 0.55, and 0.50 amperes, respectively. Different settings gave other, but not widely different, values. In the case of Zn, at 1.7 amperes, a high resistance state occurred—equivalent to the establishment of a high resistance at the contact. The current fell to 3×10^{-3} ampere, and the direction of rectification changed to A. Magnetite against Al, Zn, Pb, and Pt, showed similar change of direction for currents from 0.5 to 0.8 ampere. The effect was not observed with Cu. Galena gave results of less certainty, although the direction was B with all the metals, Mg, Al, Zn, Cu, Fe, Sn, and Pb for two amperes.

On some occasions, immediately after reversing from the direction of larger current, the current remained large for a second or so, then falling to a low value. This was noticed at times with PbS, Ag; Te, Al; Te, Cu; Si, Pt; and Si, Zn. This lag lasted longer, the longer the current

had been maintained before reversing. The lag occurred in both *A* and *B* directions, for different substances; and the conductance fell from the value just preceding, in some cases, and rose to a higher, in others.

Often, when several amperes were passing, the current would be reduced suddenly to but a milliampere or so, at 20 volts, with the substances still in contact, and the rectification sometimes still persisting. This state, independent of the direction in which the current had been flowing, was permanent, as the substances could be pressed gently together without destroying the high resistance. The phenomenon was marked with Si against Mg, Al, Zn, Cu, and Pt; also with magnetite against Al, Zn, and Cu.

The rectification was less for small currents, after the passage of large currents, than before.

Microscopic Examination During Passage of Large Currents.

Certain light effects were observed to take place coincidently with jerks and irregularities observed with the current-measuring instruments. The most striking phenomena were obtained with silicon. A microscope of 50 diameters magnification was used. The appearance, with Pt, may be seen from Fig. 1. For the direction *A*, at 1.8 amperes and 3.8 volts the tip of the platinum wire, *a*, was dim, while the adjacent Si, *b*, was bright. On reversing, *b* became less bright, while *a* grew nearly as red as *b* after the lapse of about 0.5 second. The voltage simultaneously rose from 3.5 to 3.8 volts, the current remaining closely the same. This was repeated at least a dozen times. With increase of current, the

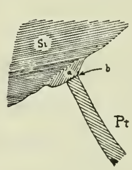

Fig. 1.

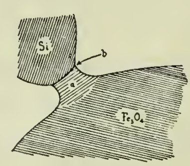

Fig. 2.

contact "broke down," and gave about the same current for each direction. With another setting, Si, Pt gave no rectification although the contact appeared brighter for the direction *A*. On the other hand, certain contacts gave rectification but no light; *e. g.*, sometimes Si, Zn and Te, Pt.

The contact Fe_3O_4, Si had the appearance shown in Fig. 2. For the direction *A*, with current of 1.2 amperes at 11 volts, the region *a* became red, the light spreading quickly from the junction, *b*, between the Si and Fe_3O_4. On reversing, blue sparks appeared for an instant along

the line b, when the current fell to 6×10^{-3} amperes at 24 volts. These changes could be repeated. Curiously, there were sparks for an instant on closing the circuit in the direction B, and also in the direction A, even if the circuit was opened for five minutes before reversing.

If, after breaking the circuit in the direction A, connection was made with a milliammeter, a sudden throw of 50 divisions was obtained, falling at once to 15, and thence slowly to about 2. A very short application of the larger current gave a throw indicating 15 milliamperes—the fall being more gradual. Increase of the larger current destroyed the rectification.

A contact of Fe_3O_4, Al showed blue sparks for the direction A, followed by redness of the metal. For current in the opposite direction, the metal was less bright, and the mineral at the contact glowed white hot. In one experiment, with a current of one ampere, a bright spot moved slowly around, a short distance from the center of the contact. With Pt, the current for A was fairly steady, while that for B was unsteady, and lowest during sparking.

Tellurium, with Mg and Al, gave continuous sparking for the direction A, and but a single spark on closing the circuit in the direction B. With Pt, however, asymmetry was obtained without sparking even at 1.5 amperes. Arc-carbon gave less definite results. Al generally gave sparking and less current for the direction B. Sometimes with Fe there was sparking only for current in the direction B. At other times there were occasional flashes for both directions. Carbon against Si, with currents of two amperes or more, gave intermittent sparking for both directions, the direction of greater current being uncertain. The direction was also uncertain for C, Fe_3O_4, but although there was not continuous sparking for the direction B, the sparks were usually larger for this direction of the current.

With PbS the light did not appear continuously, and experiments made to determine the light effect were therefore uncertain. The sparking usually took place, however, in the direction B.

In a number of special experiments, the effect of large currents could be seen without the aid of a microscope. A small cube of PbS, placed between the ends of two No. 50 aluminium wires grew red hot and showed blue sparks where the current entered, the metal being redder on this side, also, when a current of two amperes was passed through. Increase of current made the sparking more energetic, and when 4.5 amperes were reached, the high resistance state previously mentioned was produced. A small piece of Fe_3O_4 placed between the wires behaved in a similar manner,

except that it was more difficult to keep the current flowing. In a similar experiment with Si, the element grew red hot, with a much brighter point where the current entered.

A peculiar effect was also obtained when two pieces of silicon, one or two cm. long, where placed in contact and a current of one or two amperes passed through the junction. The piece on the negative side, even if thinner, was brighter from the contact to a cm. or more away. A small blue spark appeared on separating the two pieces, and it was found impossible to produce an arc. After the experiment the pieces were fused together. The effect disappeared when sufficiently large currents, *e. g.*, 25 amperes, were passed through the junction. This was very different from the behavior of two pieces of Fe_3O_4 in contact, in which there was usually no sparking, or difference in color on reversing. Once, when rectification appeared at 3 amperes, with the greater current in the direction A, the contact appeared redder as a whole when the current passed in this direction.

Effects in High Vacua.

The foregoing experiments, while suggesting electrolytic, or allied, action, at least made certain the necessity of performing the experiments with chemically clean surfaces. For this purpose a number of methods were tried. First, an attempt was made to clean the substance by using it as a cathode in a discharge tube, and causing it to give off a cathode deposit. The result was unsatisfacotry, as the effect was uncertain—a result which is in accord with the literature of the subject. Melting the substance by passing a heavy current through a piece in which was a narrow portion, was found to present too many difficulties. Cutting the specimen by means of cut-nippers operated through a ground joint was found too complicated to be practical.

The method finally employed was a simple one, and may be understood by an examination of Fig. 3 (*a*). The first step in the procedure was to exhaust the system by connecting the ground joint, J, with a Gaede mercury pump. When the highest vacuum the pump would give (without freezing mixtures) was attained, tested qualitatively by the discharge tube, the cock was closed and the system removed from the tube leading to the pump. In the first experiments, the cock was not used—the tube being sealed off—but the vapor of the vacuum wax used was later found not to give different results from those obtained with sealing. The substances studied had previously been set in solder, if poorly conducting, and placed in a holder, as (*b*), Fig. 3. In the figure is shown a metal, filed into the required shape, and held in place by a screw. This holder,

containing a piece of iron wire (shown dotted), could be moved from the outside by a 6-inch permanent horse-shoe magnet; and as this wire was placed off center, the holder could be rotated through any angle. A continuous electrical connection between the holder and the electrodes in the end of the tube was secured by soldering to them a closely-wound coil of No. 48 bare copper wire, about 1/8 inch in diameter. The holder could be moved with ease where desired, and as many as four specimens could be kept in the bulb, B_1, without serious entanglement.

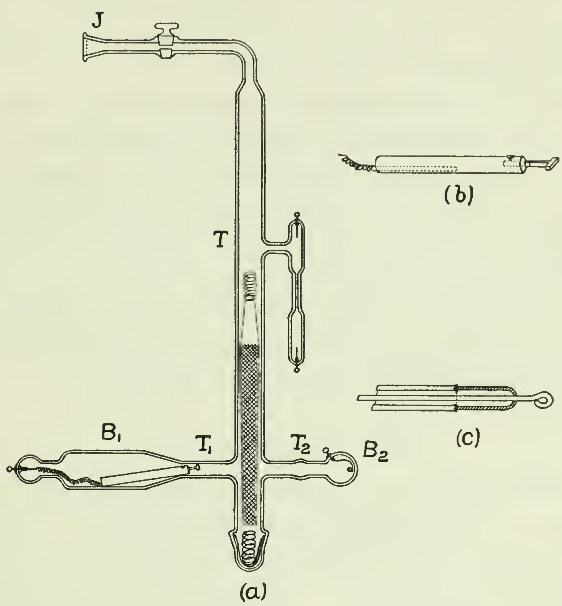

Fig. 3.

The specimen could be cleaned by filing, in which case it was allowed to rest against the file, the holder being in the tube, T_1, and the whole system was shaken back and forth to permit motion of the file relatively to the specimen. The file, of circular section, was prevented from breaking through the tube by a spring fastened to the top, and another spring, one end of which was pulled out, bent into the form of a U, and placed in the tube with the ends of this U pressing into two dents in the wall of the tube. This served to keep the spring in place.

Another method of securing a fresh surface, more satisfactory than by filing, was to break off the end of the specimen by dropping the file upon it as it protruded from the side tube, T_1. This was facilitated by filing a small indentation in the specimen near the holder. Metals were bent back and forth until they broke, by turning the holder through 180°

before each impact. In this way, with a soft metal like aluminium, a clean surface 1 mm. square could be obtained. Of course, before placing specimens in contact, the tube T was inverted so that the file did not hinder passage from T_1 to T_2. In the figure is shown a small bulb, B_2, containing tellurium in contact with a platinum wire which served as electrode. Owing to the comparatively low melting point of tellurium, it could be melted, in vacuo, through the glass. Substances which had to be broken or filed were contained in another bulb, similar to B_1, which was fastened to the tube, T_2, after B_2 had been removed. To get at any holder or specimen it was, then, merely necessary to cut off the tube at the point where the letter T_2 is situated.

In order to use, in some experiments, a much larger current than ordinary vacuum-tube electrodes will stand, the special electrodes shown in Fig. 3 (*c*) were made. A ring of platinum foil was fastened to the glass tube by means of soft blue glass. This platinum was then copper-plated, and a short lead tube, into one end of which a stout copper wire had been soldered, was soldered to the coppered platinum. Such an electrode was capable of holding a Crookes vacuum, and the amount of current was limited only by the size of the copper wire. This method of soldering lead to platinum was taken from Strasser.[1]

Results in Vacuo.

The substances used in the apparatus just described were Mg, Al, Fe, Pb, against Te, Si, galena, and natural graphite. In the open air, Te and the common fused Si gave good rectification for each metal, in directions B and A, respectively. The effect was strongest with Mg, Al, and Fe. With considerable pressure on a clean Mg surface, Te gave once a small preponderance of current in the direction A. The other substances, galena and natural graphite, gave rather uncertain action at best—the currents in the two directions often being equal—but such rectification as was obtained was usually in the direction B except with PbS, Al and PbS, Pb. The thermo-E.M.F. of these metals was from carbon to metal through the junction. Two kinds of silicon were used: the common fused silicon and some pure crystals, obtained from Eimer and Amend and Bausch and Lomb. The former always gave rectification in the direction A, while some crystals gave rectification nearly always in the direction B. The pure crystals were about 3 mm. long and not more than 0.3 or 0.5 mm. in thickness. The fused silicon was broken into pieces of about this size, and both set in solder. The thermo-E.M.F. for both kinds of silicon was the same; *i. e.*, Al to Si through the junction.

[1] B. Strasser, Ann. der Physik, 31, pp. 890–918, 1910.

With currents and voltages of from 10 to 50 milliamperes and 1 to 3 volts, the following effects were observed in vacuo. Tellurium showed the same action with all the metals tried. Before the metal had been filed, the rectification was the same as in air. Afterward, the currents were exactly equal for a given contact and for those in the immediate neighborhood. There was often a slightly greater current for *A*, the direction opposite to the rectification in air, giving rise to an E.M.F. difference of 0.01 to 0.04 volt, *in the direction of the thermo-E.M.F.* This held good at 40 or 50 milliamperes or more. For some contacts there was rectification in the direction *B*, of the order of 5 or 10 per cent. of the total current. Whenever a part of the metal which had not been filed or broken touched the tellurium, marked rectification appeared. The possibility of there being a short circuit was eliminated by touching the platinum wire leading to the tellurium, when the current was very much increased. Experiments in which the tellurium was broken or melted, and the metals broken or filed, all gave the same results. This held good even when the contact was one of considerable resistance. The only metal that gave uncertain action at times was aluminium. Magnesium, on the other hand, gave at all times consistent results. The probable reason is that the former contained traces of silicon, for on dissolving it in aqua regia, a small brownish residue remained, insoluble in hot aqua regia or in hot dilute nitric acid. The magnesium, on being dissolved in hydrochloric acid, gave no visible residue.

The pure silicon gave rectification in direction *B* to a small extent, and at times gave none at all, whereas the fused silicon usually gave considerable rectification in the direction *A*, very rarely giving as low a difference as 0.1 volt, and never giving the same current for the two directions. The resistance, also, was usually above that for the contacts with pure silicon. The test with pure silicon was difficult, as it was hard to break off the ends of the small, needle-like, crystals without making the fracture close to the surface of the solder.

Rectification with galena was uncertain, as in air, but more current was obtained in the directions *A*, *B*, and *A*, with Al, Fe, and Pb respectively. With graphite there was no rectification with any metal, save for occasional slight differences in either direction. In all the foregoing experiments, the tests were made with slow reversals.

Some of these experiments were so suggestive of an action due to a resisting film of oxide, especially those with tellurium, that experiments with melted tellurium were carried out in air, as a check upon the work. When a current of 2 amperes at 10 volts was passed through tellurium, melted in a quartz tube, with Pt and Al electrodes the current quickly

fell—when the direction was that of higher resistance—to about ½ ampere. On opening the circuit and closing it again, the value was still ½ ampere, but if the circuit was opened, and 1.5 volts applied in the same direction, the current was too small to give a readable deflection; *i. e.*, < 0.0002 ampere. On reversing, however, the deflection grew slowly until it reached 8×10^{-3} ampere. The large current, passed in the opposite direction, resulted in a deflection at once, on applying the smaller E.M.F. in the same direction.

When the quartz tube was placed in a thermostat, and the aluminium wire broken off under the surface of the melted tellurium, the results were not very satisfactory owing to the heat conducted away by the aluminium wire. On one occasion, however, the current was sensibly the same in both directions, but rose in the direction B, and fell in the other direction. A more satisfactory arrangement was had by melting a piece of tellurium in the open air, on a piece of sheet aluminium hammered into the form of a shallow dish. As the tellurium melted, a small quantity of greenish fumes was given off, after which it remained quiet, "wetting" the aluminium surface. When a platinum wire touched the melted tellurium, and a current was passed through, it was found to be steady and closely the same for both directions. The resistance rose somewhat when the substances were cooled. An aluminium wire touching the solid tellurium now formed a rectifier—the contact with the sheet aluminium serving as a low resistance contact. When the whole was heated the aluminium wire gave good contact, and when the drop of tellurium was lifted by means of it, and replaced, rectification was obtained in the direction opposite to that just preceding.

Experiments in Various Gases.

Contacts, not chemically clean, carrying small currents showed no loss of rectification when placed in various gases. With large currents, certain effects were observed. In nitrogen there was less bright illumination than in air; *e. g.*, with Te and Al or Mg. Oxygen gave brighter illumination than air, and Mg in contact with Te was ignited by a sufficiently heavy current.

A three-way cock in the system of tubes connected with the Gaede pump made filling the apparatus, Fig. 3 (*a*), with gas a simple matter. The system was exhausted to a Crookes vacuum, while the gas in question passed from the generator and purifying tubes, through the three-way cock. The cock was then turned to permit the flow of gas into the system at any rate desired. After removing the apparatus from the pump, the specimens were broken off or filed as previously described.

Hydrogen.

Hydrogen was made by electrolysis of KOH solution in a water voltameter and was dried by being passed through a tube containing glass beads and phosphorus pentoxide. Tellurium showed rectification of one or two hundredths of a volt in the direction B with all the metals, except once when Pb showed a small preponderance of current in the direction A. Fused silicon showed rectification for A, with all the metals. Carbon gave currents nearly the same for the various metals, while galena usually gave the greater current for B with Al, and A with Fe, although in the latter case the readings were often the same, as was the case with Pb.

Carbon Dioxide.

Carbon dioxide was generated by the action of hydrochloric acid on marble, purified by passing through potassium hydroxide solution, and dried with phosphorus pentoxide. Tellurium gave usually the same current in the two directions with all the metals, there sometimes being a difference in favor of the direction B of one or two hundredths of a volt. The difference, before filing, amounted to tenths of a volt. Fused silicon gave rectification in the direction A with every metal. Galena gave much the same values of current, with all the metals, there being rectification in the direction B for some contacts with Fe. Graphite, also, showed no rectification except a few times for A with Al and Fe.

Nitrogen.

Nitrogen was produced by heating a solution of ammonium chloride and sodium nitrite. It was cleaned by passage through chromic acid and potassium hydroxide solutions, and dried with phosphorus pentoxide. Tellurium showed currents in the two directions with Fe at various currents. The same held with Pb. The currents were the same for Al, with an increase in the direction B for some positions. Magnesium gave equal currents, and currents greater for B or A, depending on the position. The pure Si (Bausch and Lomb) gave the same current in both directions, while the potential varied as much as one hundredth of a volt. This held good for Al as well as the other metals. The fused Si, on the other hand, gave definite rectification in the direction A, being especially large with Al. Galena against Mg and Fe gave greater current in the direction A, Al in the direction B, while with Pb, the currents were either equal, or that for A was greater. With graphite the currents in the two directions were equal, except for occasional increases for A with all four metals.

Oxygen.

The oxygen was prepared by heating equal parts of pure potassium chlorate and manganese dioxide, and was freed from any moisture by passage through phosphorus pentoxide. An escape tube, extending several centimeters into mercury was provided to guard against excessive pressure. Tellurium (previously melted in vacuo) with oxygen gave rectification with Mg and Al as well as in air, after a few reversals. The same held true for Fe and Pb, but to a somewhat less extent. Pure Si gave more or less rectification in the direction B, for various values of current, although sometimes the currents were the same. Fused Si rectified in the direction A with all metals, and all contacts except once with Fe when both currents were equal. Galena gave rectification in the direction B, strongly with Mg and Al, usually with Fe, and more or less with Pb. With graphite, the currents were sometimes in the direction A and sometimes equal; Pb gave, occasionally, a greater current in the direction B.

Conductivity of Metal Filings in Air.

As a check upon the previous work, a study was made of the conductivity of metal filings in air and in vacuo. Eccles[1] observed that the coherer does not obey Ohm's law, and the writer[2] has found asymmetry with the coherer, although the phenomenon is not so definite nor so easy to obtain as the deviation from Ohm's law. A case of asymmetry with two copper wires[3] has already been mentioned.

In the present experiments, filings of copper, aluminium, and iron, produced and studied in air, were first examined. The deviation from Ohm's law is considerable, Fig. 5 (*a*) and (*b*). Asymmetry was observed with each of these metals, the current being as much as 45 per cent. greater in one direction than in the other. If the current were kept in one direction for some time, the conductivity rose, but fell in the other direction, as could be seen by making occasional reversals. Aluminium did not show this last effect well, and, in fact, needed considerable pressure to have current flow at all.

Apparatus for Producing Metal Filings in Vacuo.

In order to produce and examine, in vacuo, a sufficient quantity of filings, the apparatus shown in Fig. 4 (*a*) was designed. A file fastened by a joint to an iron rod, to increase the inertia, was enclosed in a long glass tube, T, with springs to prevent the file breaking through the ends

[1] Eccles, Electrician, 47, pp. 582, 715, 1901.

[2] R. H. Goddard, Phys. Rev., 28, p. 411, 1909.

[3] Shaw and Garret, Phil. Mag., 8, p. 164.

of the tube. To this tube were attached various other tubes: a Crookes tube to test the vacuum, and a tube, T_1, one end of which could be attached by the ground joint, to the Gaede pump, while the other end—joining T—supported the specimen to be filed, shown enlarged, Fig. 4 (*c*).

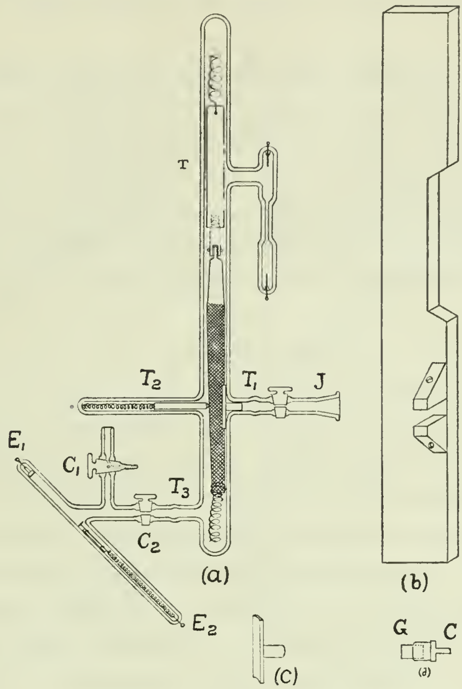

Fig. 4.

In order to press the file against the specimen, an iron rod and a spring were placed in the tube, T_2, the rod being provided at the end with a steel ball, which pressed against the file.

To produce filings, the apparatus was placed on the board, Fig. 4 (*b*) so that T_1 rested in the notch of (*b*), as near the junction with T as possible, and the whole was shaken back and forth. With this method of holding the apparatus there was no shearing stress on the glass, and filings could be obtained almost as rapidly as with a vise in air. In practice, however, the rate was not made excessive, for fear of heating the specimen, and thereby breaking the glass.

When a sufficient quantity of filings had been produced, the tube, T, was turned until the filings dropped through the tube, T_3, into a kind of coherer, in which the conductivity could be tested by means of the electrodes E_1 and E_2. These electrodes were of copper, of a size to fit the glass tube, with platinum foil soldered to the faces to give good

contact. The electrode, E_2, was connected to the platinum leading-in wire with a fine, flexible spiral of copper wire, and could be moved from outside the tube by a magnet. Small quantities of hydrogen and oxygen, produced electrolytically, and dried with phosphorus pentoxide, could be admitted to this coherer by way of the three-way cock, C_1, after C_2 had been closed.

In taking the apparatus apart it was necessary simply to open the upper end of T, and cut off T_1 and T_3 at the points where the letters, T_1, and T_3, are placed. When the file and specimen were introduced or removed, the rod holding the steel ball was pushed out of the way by a stiff wire, inserted between the specimen and the wall of T_1, the end of the wire engaging the crimp that held the ball in place. After each experiment, all filings were removed from the tubes and the surface of the file.

Conductivity of Metal Filings Produced in Vacuo.

With copper, in vacuo, there was no asymmetry, nor change of conductivity with time, nor deviation from Ohm's law as observed in air—there being, in fact, a slight falling-off of current[1] with E.M.F., Fig. 5 (*c*). Occasionally, however, as the voltage was increased in steps of about 1/500 volt, the current jumped to a higher value, thereafter obeying the same law. This is in agreement with the theory of Eccles that deviation from Ohm's law is due to turning of the irregular particles under the influence of the electrostatic field, thus furnishing more contacts at higher voltage. It shows, further, that a film is necessary, to prevent fusions, *i. e.*, good contacts, before this turning can occur. Sparks from a Hertz oscillator several feet away reduced the resistance to a low value.

When oxygen, prepared as above described, was admitted, the resistance increased about 25 times, the deviation from Ohm's law appeared, Fig. 5 (*d*), and asymmetry was observed, there being a tendency for the conductivity in the direction in which the current was flowing to be higher than in the other direction, as in air. When, however, hydrogen was admitted to the copper filings produced in vacuo, there was no noticeable asymmetry, and the current-voltage characteristic, Fig. 5 (*e*), was the same as in vacuo. On removing the hydrogen by opening the cock, C_2, and then admitting oxygen (repeating the operation several times, to remove all the hydrogen) deviation from Ohm's law appeared, Fig. 5 (*f*). In all experiments, the filings were, of necessity, moved about when gases were admitted.

[1] The resistance of the coherer has been found to increase with increasing temperature, owing, probably, to expansion and breaking of some of the contacts. This may account for the deviation in vacuo, if increased heating, due to increasing the current, can produce the same effect.

Aluminium and magnesium did not give results so satisfactory, as a certain amount of pressure was required to give conduction—though much less than that required in air or oxygen. Aluminium filings produced in vacuo, gave deviation from Ohm's law as with copper—Fig. 5

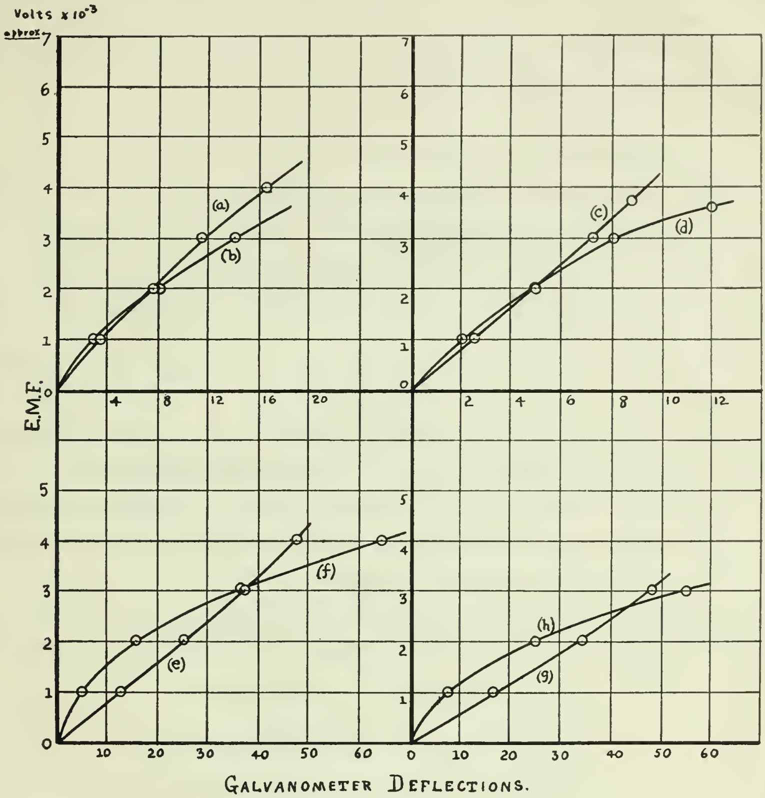

Fig. 5.

(*a*) Copper, in air; (*b*) iron, in air; (*c*) copper, in vacuo; (*d*) copper, in oxygen after vacuum; (*e*) copper, in hydrogen after vacuum; (*f*) copper, in oxygen after hydrogen; (*g*) aluminium, in vacuo; (*h*) aluminium, in vacuo.

(*g*); although occsaionally as (*h*), which, since pressure is necessary for conduction, is easily explained by turning of the particles. No asymmetry was observed. When oxygen was admitted the resistance increased greatly, and the deviation from Ohm's law was large. Hydrogen, acting on filings produced in vacuo, necessitated a little greater pressure for conduction, gave deviation from Ohm's law as in vacuo, and no asymmetry.

It was thought that impurities in the aluminium might necessitate the application of pressure, but it was found that magnesium filings required pressure at all E.M.F.'s, even when no ground joints, *i. e.*, vacuum wax, was used. Magnesium behaved in other respects like aluminium.

Odor of Aluminium and Magnesium Filings.

It may be of interest to note, in passing, that the filings of aluminium and magnesium, when produced in vacuo, gave a strong odor somewhat resembling garlic even when the tube was not opened until over a week after performing an experiment; and the odor in the tube still persisted a day or so after air was admitted. A piece of either metal, filed in the air, lost its odor in less than half a minute.

Conductivity of Galena, Powdered in Vacuo.

In order to test whether or not the peculiarities of conductivity across contacts of chemical compounds depend upon the surrounding gas, galena was filed in vacuo, and the resulting powder examined. The apparatus was similar to that shown in Fig. 4 (*a*), except that there were no cocks, C_1 and C_2.

The galena, Fig. 4 (*g*), was first set in a block of solder, after which this block was soldered to a piece of copper, turned in a lathe to the form shown in section, (*c*). This was fastened to the holder previously described, Fig. 3 (*b*), and in place of a spring to furnish pressure of the file on the galena, a lead rod was placed in the tube, back of the holder, so that the pressure of the galena on the file could be varied by varying the angle at which the apparatus was held.

In air, galena filed to a powder, showed deviation from Ohm's law, Fig. 6 (*a*), and asymmetry—there being a difference in conductivity

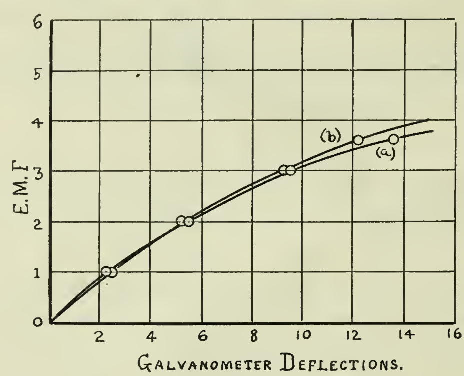

Fig. 6.

Powdered galena. (*a*) In air; (*b*) in vacuo.

of 10 to 15 per cent. for the two directions. The conductivity in the direction of an applied steady current increased faster than that in the opposite direction, observed by reversals, independent of which conductivity was the greater. In vacuo the deviation was still present,

Fig. 6 (*b*), together with asymmetry of the same nature and magnitude as in air.

Oscillograms of Rectifiers at High Frequencies.

The foregoing experiments show that a film of some sort is necessray to produce peculiarities of conduction at contacts, and it remains to determine how such a film acts. The experiments which follow have thrown some light on this question, although not as much as was anticipated. It has already been shown by Pierce[1] that no effect is present for a time longer than 1/6,000 of a second that is not accounted for by the voltage-current characteristics of the rectifier for steady currents. In view of the fact that crystal detectors are being used as receivers of waves of 200,000 or more frequency, and further as Merritt[2] has demonstrated that the silicon detector will act for a wave-length as short as 15 cm., it seemed advisable to obtain oscillograms for frequencies of several hundred thousand, if possible.

Apparatus.

The method will be understood by an examination of Fig. 7. A Poulsen arc was used to produce the high-frequency oscillations, as being the best means of producing a continuous train of undamped oscillations, except by using a high frequency alternator. The arc was on used by Dr. Story[3] in a research on the Poulsen arc. A resistance, P_1, and an inductance, not shown, were in series with the arc. In the high frequency circuit was a variable oil condenser, C, and an inductance consisting of three coils, S, S_1, and S_2, of the same shape and size. These were arranged so that all the current passed through S and a variable carbon resistance, P_2, and then branched, part of the current going through a group of rectifiers in parallel, R_1 and the coil S_1, and the other part, through an equal number of rectifiers, R_2, arranged so as to give rectification in the opposite direction, and thence through the coil S_2. The coils

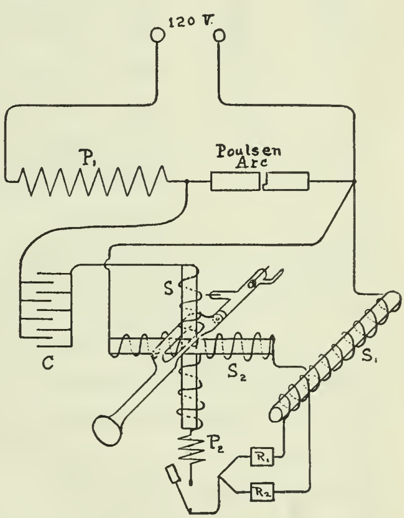

Fig. 7.

[1] G. W. Pierce, Phys. Rev., 28, pp. 153–189, 1909.

[2] Ernest Merritt, Phys. Rev., 32, p. 630.

[3] W. E. Story, Jr., Phys. Rev., 30, pp. 236–261, 1910.

S and S_2 were made to act at right angles to each other, on the beam of cathode rays in a Braun tube, whereas S_1 was a dummy coil. It is easily seen that the total current in the circuit remained the same, for if the rectifiers R_1 hindered the passage of current through S_1, the rectifiers R_2, acting in the opposite direction, would let current through S_2, and vice versa. The rectifiers were made as follows: a large number of pieces of the crystal, to which there was good contact (*e. g.*, by setting the pieces in solder, or clamping them under brass plates) were fastened to a board. A groove was made around the rectifiers, near the edge of the board, and holes were drilled at intervals in the bottom of this groove. Contacts were made by inserting wires in the holes, and bending them until they touched the crystals. After all the wires had been separately adjusted the groove was filled with mercury, thus connecting the wires in parallel.

The Braun tube, made by the writer, was of the special form shown in Fig. 8. The cathode beam was produced by a hole about 1/3 mm. in diameter, in an aluminium disk shown in section, P_1. In this disk was another, larger, hole to facilitate exhaustion of the tube. The rays passing through this second hole were stopped by the aluminium disk P_2. Deflection took place in the tube, t, which was but 2 mm. inside, and 3.3 mm. outside, diameter. A larger tube, T, served to strengthen the apparatus and aid in evacuating the tube. The screen S was made by spreading powdered willemite, mixed with alcohol, on the inside of the bulb and letting it dry—after J. J. Thomson. The part of the main tube below T and t was covered with tin foil and connected, with the anode, to earth. The distance from P_1 to S was 40 cm., and a current of 0.3 ampere in one of the coils gave a deflection of 6 mm. In practice, the current varied from 0.3 to 0.7 ampere.

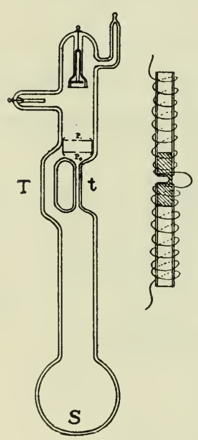

Fig. 8.

Each coil was a single layer of cotton-covered copper wire, 0.5 mm. in diameter, wound on a glass tube, 1.22 cm. in diameter, and soaked in melted paraffine. They were 20 cm. long, with 17 turns to the cm. In order to bring the two halves of these coils as near the tube, t, as possible, they were held in place by the notched plugs of wood, shown in section in the figure.

Instead of using a high potential storage battery, it was found possible to use a Wimshurst electric machine, with or without a condenser in parallel, provided a high resistance formed by a pencil mark on ground glass, was placed in series. With the proper resistance (not easy to get)

the cathode beam was extremely steady, and the glow in the tube persisted for a minute or more after stopping the machine. Lines ruled on paper with india ink[1] were more satisfactory.

Experimental Results.

The oscillogram, a Lissajous' figure, shown in Fig. 9 (*a*),was obtained with silicon against steel, under exceptionally good circumstances. There were 30 contacts in each group, R_1 and R_2, and the calculated frequency was 410,000. The phenomenon could be repeated as many times

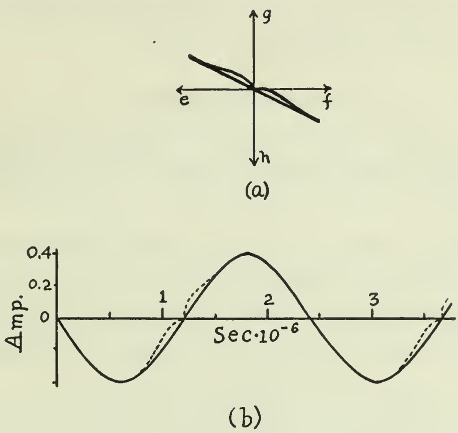

Fig. 9.

f, direction of total current; *g*, direction of greater rectified current; *h*, direction of lesser rectified current. Frequency 410,000.

as desired, but the arc did not remain steady longer than two or three seconds, too short a time, it was found, to affect a photographic plate. The failure of the arc to give oscillations for a longer period was no doubt due to the comparatively large resistance of the groups of rectifiers. At other times these curves were only feebly approached, which was true also, of the same number of contacts with copper, molybdenite and aluminium, tellurium.

The conclusions which are indicated are shown in Fig. 9 (*b*), where the deviation is from a sine wave form instead of the straight line in the Lissajous' figure. There is, apparently, an opposition to the current, or a back E.M.F., which appears for about 4×10^{-7} second, followed by an increase in current lasting the same length of time, when the current is reversed. It strongly suggests a crowding of ions against the film, and the springing-back of these ions at the instant the current is reversed.

[1] F. A. Aust. Phys. Rev., 32, pp. 732–733, 1911.

Criticism of the Experiment.

It seems likely that important information could be obtained by using a high-frequency alternator, thus making it possible to obtain photographic exposures of a minute or more. Perhaps, also, more persistent oscillations could be had with the arc by using a great many contacts in parallel, to reduce the resistance. In either case a large number of contacts would be necessary, each adjusted for maximum rectification, and for equality with the other contacts as to current in both directions. If the voltage were considerable, it might be necessary to place several of these groups in series. A smaller hole in the diaphragm, P_1, could be used to advantage, with a long exposure.

Conclusions.

1. Pure elements give little or no rectification against pure metals, unless oxygen (or an active gas) is present. The evidence in support of this is as follows:

(*a*) Pure tellurium and pure silicon give practically no rectification against metals, in vacuo, hydrogen, nitrogen, and carbon dioxide, but behave in oxygen as in air. The conclusion is also supported by the action of an aluminium wire broken off under melted tellurium. Natural graphite is at best uncertain for slow alternations.

(*b*) A piece of tellurium, melted in air in contact with a piece of aluminium, shows unilateral effects or not, depending upon whether or not the tellurium adheres firmly enough to "wet" the aluminium surface.

(*c*) Copper filings in the form of a coherer, produced and examined in vacuo or hydrogen, show no asymmetry, and deviate from Ohm's law with an upward slope, but in oxygen give the well-known deviation observed with filings produced in air. Aluminium and magnesium do not, however, show such conclusive behavior.

(*d*) Currents of 0.5 ampere or more, in air, give evidence that whatever unilateral effects appear are due to the presence of oxygen, for the following reasons: the direction of greater current, for sufficiently large current, is from metal to substance regardless of the direction for small currents. This is the direction for tellurium for all currents; and this element, by (*a*), rectifies owing to the presence of oxygen. Further, for large currents there appear incrustations, with colors characteristic of the oxides of the substances used. The current in the direction of metal to crystal is the more unsteady, for large currents, as it is with tellurium.

2. Rectification, other than that due to the presence of oxygen, occurs at contacts of impure elements or chemical compounds.

(*a*) Impure, fused, silicon rectifies under all circumstances.

(*b*) The behavior of galena in air and vacuo also lends support to this conclusion, although it is, at best, an uncertain rectifier.

(*c*) Galena, filed to a powder in vacuo, shows deviation from Ohm's law exactly as in air. The deviation is of the same character as that observed previously by the writer for many other powders in air, the effect appearing under all circumstances except when the powders were subjected to great pressure.

(*d*) Chemical compounds, in air, usually rectify in the direction opposite to that with pure elements in air or oxygen.

3. The phenomenon is due, primarily, to the presence or formation of a film at the contact.

(*a*) Pure elements require the presence of oxygen (therefore of oxide) at the contact.

(*b*) The resistance of copper filings produced in vacuo increases 25 times on admission of oxygen. A similar change takes place with aluminium and magnesium filings.

(*c*) In many cases, with large currents, the current remains large, for a second or so, after reversing to the direction of lesser current. This indicates that the building-up of resistance requires a certain amount of time.

(*d*) In the experiment with melted tellurium, with large current, a small E.M.F., after application of a larger E.M.F., both in the direction of greater current, gave practically no current, but gave 0.008 ampere on reversing. This was evidence of a deposit which the small E.M.F. could gradually remove *if applied in the direction of greater current.* Also, since 10 volts gave ½ ampere, while 1 volt gave no readable deflection, there is evidence that the larger current kept flowing either because the heat developed, or the E.M.F., or both, continually broke down the film.

(*e*) The experiment with Fe_3O_4, Si, large current, in which a single spark was visible (microscopically) when the current was passed in the direction of lesser resistance, five minutes *after* the circuit had been broken with the current in the direction of higher resistance, indicates the breaking-down of a resistance at the contact. The continued sparking in the direction of higher resistance, at large currents, with this and other contacts, indicates that the irregularities observed for this direction, A, are due to breaking down and sparking. Further, the changes in brightness of the substances and metals, on reversal of current, are indicative of changes in the place of greatest heat production, or changes in heat conductivity, but are not so easy to interpret as the following special experiments.

(*f*) When galena, Fe_3O_4, or silicon were placed between the ends of two aluminium wires, and a current of two amperes passed through, blue sparks appeared and the metal was redder, on the side the current entered the crystal. The entire substance was red hot. In this case a comparatively large region was heated, and if oxygen was deposited, as might be expected, on the anode wire, more heat should be generated, owing to greater resistance, at this surface. Hence the metal should be redder, as was observed. Continued sparking showed continued breaking down of the film—presumably of oxygen with Fe_3O_4 and silicon, and of sulphur with galena.

On the other hand, in the experiment in which a large current was passed through a small contact between two large pieces of silicon, the silicon on the side at which the current passed *from* the contact was redder. The probable explanation is that a *small* region was heated, owing to the very refractory nature of silicon, and that the heat generated in this small region passed more easily to the piece of silicon on which there was no film of oxide, since the thermal conductivity of the film was probably small compared with that of the hot silicon.

(*g*) The experiments mentioned at the beginning of the paper, concerning the change in resistance of rectifiers measured by a very small current, after a current of about 10^{-2} ampere had passed through the contact are indicative of the building up of some sort of permanent resistance, but the data do not show sufficient regularity to enable further conclusions to be drawn.

4. Solid rectifiers are, apparently, analogous to the aluminium valve, or electrolytic rectifier. In this rectifier a solid film is produced and large ions are packed against it, giving a back E.M.F., when the current passes in one direction, whereas smaller, negative, ions pass freely through the film when the current is in the opposite direction. The greatest point of dissimilarity is the continued breaking down of the resisting film, in the case of solid rectifiers, probably due to heating.

(*a*) The hysteresis effect observed by Pierce with carborundum, for the first few reversals, together with the fact, observed by the writer, that tellurium cleaned in vacuo required a few reversals before showing good unilateral effect, when oxygen was admitted, are both analogous to the slow building up of resistance with direct current, for a fresh plate in the aluminium valve, before an alternating current has been applied.

(*b*) The oscillogram at 410,000 frequency suggests the building up of a back E.M.F., which gives a slight additional current at the moment the current is reversed. This conclusion is, however, based upon a single experiment.

Summary.

1. A large number of experiments with currents up to 9 amperes suggested the necessity of using contacts of as nearly chemically clean surfaces as possible.

2. By means of a glass apparatus which could be evacuated to a Crookes vacuum, it was possible to break or file the ends of substances and metals in vacuo, and measure the conductances. Proceeding in this way it was found that tellurium and pure silicon lost most or all of their power to produce rectification when cleaned as above, in vacuo, hydrogen, nitrogen, and carbon dioxide, but behaved in oxygen as in air. Fused silicon and galena gave rectification in vacuo and all gases; the former always, the latter often. Galena and natural graphite were found uncertain even under ordinary conditions.

3. Copper filings produced and examined in vacuo and hydrogen did not show the anomalies of conduction manifested in air and oxygen. Aluminium and magnesium gave uncertain results. Galena powdered in vacuo by filing showed the same anomalies as in air.

4. The experiment with copper filings supports the theory of Eccles, that the deviation from Ohm's law of the coherer is due to turning of the particles, due to electrostatic forces, so that the long axes point in the direction of the current. Although Ohm's law was practically obeyed, there were sudden increase in conductance on raising the voltage. There was little evidence of turning in general, however, unless a film of oxide was present—although Hertz waves greatly increased the conductance.

5. From the experiments mentioned in (2) and (3) it is concluded that rectification is of two kinds, "surface" and "body" rectification, and that the former takes place with pure elements in an active gas, and the latter with impure elements and chemical compounds, irrespective of the nature of the gas present.

6. Many experiments with contacts in air carrying large currents, and contacts in vacuo, showed phenomena which suggested that a film of some sort is necessary in order to have rectification. These experiments, together with an oscillogram of a number of silicon, steel rectifiers in parallel indicate that the action of the solid rectifier is like that of the aluminium valve, or electrolytic rectifier; *i. e.*, a film is formed which hinders the motion of certain ions—with this difference, that, in solid rectifiers the film is broken down by heat, or sparking, so that some current usually flows in the direction of higher resistance.

Clark University,
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